5.(2)
AUTHORS: Sheka, I. A., Voytovich, B. A.,   SOV/78-4-8-16/43
              Nisel'son, L. A.

TITLE: On Compounds of Pentachlorides of Niobium and Tantalum With
              Phosphoroxychloride (O soyedineniyakh pentakhloridov niobiya
              i tantala s khlorokis'yu fosfora)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 8,
              pp 1803 - 1808 (USSR)

ABSTRACT: The investigation of the systems $NbCl_5$ - $POCl_3$ and $TaCl_5$ -
              - $POCl_3$ is of practical importance since the distillable re-
              action products of these systems may be used for the separa-
              tion and the purification of tantalum and niobium by rectifica-
              tion (Ref 1). The phase equilibria crystal - liquid and liquid-
              vapor were investigated. In contrast to the phosphoroxy chlo-
              ride compounds of $ZrCl_4$ and $HfCl_4$ which are characterized by
              a strong cooling, $NbCl_5 \cdot POCl_3$ and $TaCl_5 \cdot POCl_3$ crystallize well.
              Both systems form monomolecular, thermally easily dissociable
              compounds in agreement with reference 2. The melting temperature
Card 1/2   of $NbCl_5 \cdot POCl_3$ is 124.5°, that of $TaCl_5 \cdot POCl_3$ 132.4°. The

On Compounds of Pentachlorides of Niobium and
Tantalum With Phosphoroxychloride   SOV/78-4-8-16/43

liquidus curve of the tantalum system is higher than that of
the niobium system. The investigation of the phase equilibrium
liquid - vapor showed maxima at a ratio $NbCl_5:POCl_3 = 1.47:1$
and $TaCl_5:POCl_3 = 1.17:1$ (Table 4, Figs 1,2). The maxima do,
therefore, not correspond to the composition of chemical com-
pounds. This is characteristic of azeotropic mixtures. The
heats of solution of $NbCl_5 \cdot POCl_3$ and $TaCl_5 \cdot POCl_3$ are approxi-
mately 3.3 kcal/mol. There are 5 figures, 5 tables, and 3 Soviet
references.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii AN USSR (Institute
of General and Inorganic Chemistry of the AS UkrSSR). Moscov-
skiy institut tsvetnykh metallov i zolota im. M. I. Kalinina
(Moscow Institute of Non-ferrous Metals and Gold imeni
M. I. Kalinin)

SUBMITTED: April 20, 1958
Card 2/2

NEKRYACH, Ye.F. [Nekriach, IE.F.]; NAZARENKO, Yu.P.; CHERNETSKIY, V.P.
        [Chernets'kyi, V.P.]; [Babko, A.K.], akademik, otv.red.;
        ROZUM, Yu.S., kand.khim.nauk, red.; FIALKOV, Ya.A. [deceased],
        red.; FOMENKO, G.S. [Fomenko, H.S.], kand.khim.nauk, red.;
        SHEKA, I.A., prof., doktor khim.nauk, red.; GNATYUK, G.M.
        [Hnatiuk, H.M.], red.-leksikograf; POKROVSKAYA, Z.S.
        [Pokrovs'ka, Z.S.], red.izd-va; YEFIMOVA, M.I. [IEfimova, M.I.],
        tekhn.red.

        [Russian-Ukrainian chemical dictionary; 6000 words] Rossis'ko-
        ukrains'kyi khimichnyi slovnyk; 6000 terminiv. Kyiv, Vyd-vo
        Akad.nauk URSR, 1959. 204 p.   (MIRA 15:5)

        1. AN USSR (for Babko). 2. Chlen-korrespondent AN USSR (for
        Fialkov).
                        (Chemistry—Dictionaries)
                (Russian language—Dictionaries—Ukrainian)

26860

5 2200   1043, 1228 1273

S/021/60/000/008/010/011
D210/D305

AUTHORS: Sheka, I.A., and Pevzner, Ts.V.

TITLE: Reactions of zirconium and hafnium hydroxides with
              sodium hydroxide

PERIODICAL: Akademiya nauk Ukrayins'koyi RSR. Dopovidi, no. 8,
              1960, 1090 - 1094

TEXT: In the experimental investigation the author studied the com-
position of ions formed during the reaction of Zr and Hf hydroxi-
des with NaOH. The ions composition was determined by measuring
the solubility of $Zr(OH)_4$ and $Hf(OH)_4$ in concentrated NaOH solu-
tions. The experiments were carried out by saturating NaOH solu-
tions with freshly precipitated $Zr(OH)_4$ and $Hf(OH)_4$ free of Cl
ions. Samples were saturated at 35°-40^OC for 2-3 hours and then
left in a thermostat for several days at 25^OC. The authors found
that complete equilibrium was attained in solution of 5-11-N NaOH

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Reactions of zirconium and ...

after 8 - 12 hours, but with higher NaOH concentration time became longer. The solubility curves were drawn from average data of 3 - 4 experiments, obtained partly on samples of the saturation and partly after 45 days. Solubility was measured by gravimetric analysis of solutions and by radiometric measurements (Hf - 181). Solubility values for low and medium NaOH concentrations were in good agreement in different experiments; with higher concentrations (12-18N) their reproducibility was poorer. The solubility of $Zr(OH)_4$ rises at first slowly, increasing in NaOH concentration higher than 9-10N. It follows from the data that during the reaction of $Zr(OH)_4$ with NaOH, complex compounds are formed, the composition of which depends on the NaOH concentration. The solution of the above hydroxides proceeds according to the equation:
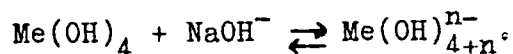
$$Me(OH)_4 + NaOH^- \rightleftarrows Me(OH)_{4+n}^{n-}.$$

The instability constant of the complex ion is expressed by the

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known equation:

$$K_H = \frac{[Me(OH)_4][OH^-]^n}{[Me(OH)_{4+n}^{n-}]}. \tag{1}$$

The solubility is expressed by the sum of metal hydroxide concentration and that of its complex anions present in the solution

$$S = [Me(OH)_4] + [Me(OH)_{4+n}^{n-}]. \tag{2}$$

Solubility data show that in NaOH solutions in the range 1 - 18N the solubility of zirconium hydroxide varies from $1.4 \cdot 10^{-4}$ to $3.1 \cdot 10^{-3}$ g of Zr. and that of hafnium hydroxide from $3.4 \cdot 10^{-4}$ to $7.1 \cdot 10^{-3}$. The concentration of $Me(OH)_4$ in NaOH solutions cannot be higher than its solubility in water; the latter can be calculated from the solubility product of $Zr(OH)_4$ in water, which is equal to $3 \cdot 10^{-26}$ [Abstractor's note: Data taken from Western li-

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Reactions of zirconium and ...

terature]; the calculated $Zr(OH)_4$ concentration in water being $1.95 \cdot 10^{-9}$. As the solubility increase of the investigated hydroxides is due mostly to complex ions formation, it follows that the concentration of $Me(OH)_4$ is about 10^5 times smaller than that of the complex ions and that the expression $Me(OH)_4$ in Eq. (2) can be omitted. It is shown that in NaOH concentrations up to ION an ion $Zr(OH)_5$ is formed an in higher concentration - the ion $Zr(OH)_6^{2-}$; further that an ion $Hf(OH)_5$ is also formed in the range of NaOH concentrations 1 - 10N. The solubility of hafnium hydroxide in NaOH solutions up to 12N is higher than that of Zr, but in higher NaOH concentrations this solubility decreases; in the author's opinion this is due to the formation of a complex compound - sodium hydroxohafnate which is precipitated from concentrated NaOH solutions: The authors obtained such precipitates from $Hf(OH)_4$ in NaOH(15-19N). In different samples of these precipitates 2.3 - 2.5

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Na atoms were present for each Hf atom; this ratio corresponds approximately to the compound $Na_2[Hf(OH)_6]$. The lower solubility of zirconium hydroxide and the absence of a maximum on its curve prove a lesser stability of the hydroxozirconate anion than that of Hf anion; this is supported by their instability constants which can be calculated from

$$lgS = nlg \ C_{OH} - lgK_H + lg[Me(OH)_4]. \qquad (3)$$

The instability constant of $Zr(OH)_5^-$ ions was found to be slightly larger than that of $Hf(OH)_5^-$ $(1.9 \cdot 10^{-5}$ and $1.1 \cdot 10^{-5}$ respectively). There are 2 figures and 13 references: 5 Soviet-bloc and 8 non-Soviet-bloc. [Abstractor's note: One reference given in Russian is a translation from German]; The references to the English-language publications read as follows: T. Taggart, Rev. Pure Appl. Chem., 1, 152, 1951; F. Venable, Th. Clarke, J. Am. Chem. Soc., 18 434, 1896; E. Larsen, A. Gammill, J. Am. Chem. Soc., 72, 3615, 1950.

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Reactions of zirconium and ...

S/021/60/000/008/010/011
D210/D305

ASSOCIATION: Institut zagal'noyi ta neorganichnoyi khimiyi AN URSR
(Institute of General and Inorganic Chemistry of the
As UkrSSR)

PRESENTED: by Yu.K. Delimars'kyyi, Academician A‡ UkrSSR

SUBMITTED: September 25, 1959

Card 6/6

S/078/60/005/010/014/021
B004/B067

AUTHORS: Sheka, I. A., Pevzner, Ts. V.

TITLE: Solubility of the Zirconium and Hafnium Hydroxides in Solutions of Caustic Soda

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 10, pp. 2311 - 2314

TEXT: The authors wanted to determine the solubility of $Zr(OH)_4$ and $Hf(OH)_4$ in NaOH and to clarify the composition of the resulting compounds. The solubility was determined at $25^{\circ}C$ in 1 - 18 N NaOH. The hydroxides were obtained from the oxychlorides by precipitating them from ammonia by means of an aqueous solution. The solutions of the hydroxides in soda lye showed no Tyndall effect. They were analyzed for NaOH, Zr, and Hf. In some experiments also Hf^{181} was used. Measures were taken to avoid the access of CO_2 to the solutions. The results are presented in a Table and in Figs. 1,2. The solubility of $Zr(OH)_4$ in NaOH at $25^{\circ}C$ is lower than that of $Hf(OH)_4$; however, with increasing concentration of NaOH it increases.

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Solubility of the Zirconium and Hafnium
Hydroxides in Solutions of Caustic Soda

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B004/B067

Also the solubility of $Hf(OH)_4$ increases with increasing concentration of NaOH; however, at 11 - 12 N NaOH it attains a maximum, and with still higher NaOH concentrations it decreases again. The composition of the solid phase separated from solutions of $Hf(OH)_4$ in concentrated NaOH (15 N and more) approximately corresponded to the formula $Na_2Hf(OH)_6$. In 1 - 10 N NaOH, the ions $Zr(OH)_5^-$ and $Hf(OH)_5^-$ were formed, whereas higher NaOH concentrations produced the ions $Zr(OH)_6^{2-}$ and $Hf(OH)_6^{2-}$. The complex hydroxo compounds of zirconium are less stable than those of hafnium. There are 2 figures, 1 table, and 5 references: 2 Soviet and 3 US.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii Akademii nauk
               USSR (Institute of General and Inorganic Chemistry of the
               Academy of Sciences UkrSSR)

SUBMITTED: July 28, 1959

Card 2/2

DUBENKO, R.G.; PEL'KIS, P.S.; SHEKA, I.A.

Dipole moments of some S-methyl derivatives of arylthiocarbazones.
Ukr.khim.zhur. 26 no.1:48-52 '60.   (MIRA 13:5)

1. Institut organicheskoy khimii AN USSR, Institut obshchey i
neorganicheskoy khimii AN USSR.
            (Carbazone--Dipole moments)

S 2200

25508

S/078/61/006/008/007/018
B121/B203

AUTHORS: Sheka, I. A., and Lastochkina, A. A.

TITLE: Reaction of potassium fluozirconate with sodium hydroxide
and ammonium hydroxide in aqueous solutions

PERIODICAL: Zhurnal neorganicheskoy khimii, v. 6, no. 8, 1961, 1868-1874

TEXT: The authors studied the effect of ammonium- and sodium hydroxide
concentrations and of the potassium fluozirconate concentration on the
composition of basic salts forming in the systems K_2ZrF_6 - NH_4OH - H_2O
and K_2ZrF_6 - NaOH - H_2O. For determining the composition of basic salts,
they used the method of changing the pH of the solution and the determina-
tion of the apparent volume of precipitations at 25°C. This method was
developed by I. V. Tananayev (Ref. 4: Izv. Sektora fiz.-khim. analiza 20,
277, 1950). It was found that in the reaction of potassium fluozirconate
with ammonia or soda lye first a basic salt of the composition
$Zr(OH)_2F_2 \cdot KF \cdot mH_2O$ was formed, and that this salt was converted into
$ZrO(OH)F \cdot nKF \cdot mH_2O$ and, finally, to zirconium hydroxide on further addition

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                                       B121/B203

of soda lye and ammonium hydroxide. Pure zirconium hydroxide was formed on
addition of 3-5 equivalents of NH_4OH or NaOH to 1 mole of K_2ZrF_6. At a

ratio $\dfrac{\text{mole}_{NaOH}}{\text{mole}_{K_2ZrF_6}} = 4.5$, the resulting basic salts were completely destroyed,

and transformed to zirconium hydroxide with very low fluorine content
(0.05 - 1 % F). A zirconium hydroxide precipitate containing 9 - 14 %
fluorine was formed with the use of ammonium hydroxide as a precipitant
at the same ratio of reacting components. Also with addition of the
8-fold quantity of ammonium hydroxide, the zirconium hydroxide precipitated
contained 2 - 8 % fluorine. The authors studied the effect of potassium-
fluozirconate concentration on the composition of basic salts and hydroxide,
and found that the zirconium hydroxide precipitated from concentrated
potassium-fluozirconate solution contained more fluorine and potassium
impurities than one precipitated from diluted solution. The precipitate
from a solution with 20 g/l K_2ZrF_6 contained 24.4 % F, from a solution

with 1 g/l K_2ZrF_6 only 11.2 % F under equal conditions of precipitation.

The degree of precipitation of Zr from solutions depends on the potassium-
fluozirconate concentration. Zr is completely precipitated from

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concentrated solutions (20 g of K_2ZrF_6 per liter) with the use of 2 equivalents of alkali hydroxide. More than 3 equivalents of alkali hydroxide are required for complete precipitation from diluted solutions (2 - 5 g of K_2ZrF_6 per liter). Basic zirconium salts are stable at pH = 5 - 9, and are converted into pure zirconium hydroxide only at pH $>$ 10. There are 7 figures, 3 tables, and 4 Soviet-bloc references.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii Akademii nauk USSR (Institute of General and Inorganic Chemistry of the Academy of Sciences UkrSSR)

SUBMITTED: February 23, 1960

Card 3/3

SHEKA, I.A., otv. red.; DELIMARSKIY, Yu.K., red.; KOZACHEK, N.N., red.; NATANSON, E.M., red.; SHEYKO, I.N., red.; MATVIYCHUK, A.A., tekhn. red.

[Applications of zirconium and its compounds in industry; materials] Primenenie tsirkoniia i ego soedinenii v promyshlennosti; materialy. Kiev, Izd-vo Akad. nauk USSR, 1962. 97 p.   (MIRA 15:7)

1. Soveshchaniye pri gosplane GNTK i Akademii nauk USSR, Kiev, 1960.
                  (Zirconium--Industrial applications)

SHEKA, I.A., otv. red.; DELIMARSKIY, Yu.K., red.; KOZACHEK, N.N., red.;
NATANSON, E.M., rod.; SHEYKO, I.N., red.; MATVIYCHUK, A.A.,
tekhn. red.

[Materials of the Technological Conference on the Use of
Zirconium and its Compounds in Industry] Materialy Nauchno-
tekhnicheskogo soveshchaniia po primeneniiu tsirkoniia i ego
soedinenii v promyshlennosti, Kiev, 1960. Kiev, Izd-vo Akad.
nauk USSR, 1962. 97 p.   (MIRA 15:4)

1. Nauchno-tekhnicheskoye soveshchaniye po primeneniyu tsirko-
niya i yego soyedineniy v promyshlennosti, Kiev, 1960.
                 (Zirconium—Congresses)

S/078/62/007/006/006/024
B124/B138

Karlysheva, K. F., Sheka, I. A.

Composition of zirconium and hafnium cupferronates

PERIODICAL: Zhurnal neorganicheskoy khimii, v. 7, no. 6, 1962, 1291-1298

TEXT: The composition of Zr and Hf cupferronates was studied as a function of the acidity of the medium and the degree of aging of the solution. Potassium fluorozirconate with 0.05% Hf (referred to ZrO_2) and hafnium oxychloride with 0.25% Zr were converted into the corresponding hydroxides, dissolved, twice precipitated with NH_3, and washed to remove the Cl and F ions. The squeezed out hydroxides were dissolved in H_2SO_4 or HNO_3 and the solutions left standing for 3-4 days. Solutions of the required concentration were then prepared from them. A freshly prepared 5% solution of cupferron recrystallized from ethyl alcohol was used. The experiments showed that neutral cupferronate of the composition $Zr[C_6H_5N(NO)O]_4$ was precipitated in the interaction of cupferron with Zr^{4+} ions, or with stable

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Composition of zirconium and ...

S/078/62/007/006/006/024
B124/B138

Fluoride complexes of Zr, sulfate, or nitrate ions (formed in solutions of an acidity 1 gr-equiv/liter) (Fig. 1). Basic cupferronates of variable composition are separated from weakly acid solutions, in which hydrolyzed and sometimes polymeric Zr ions are formed (Fig. 2). The results found for hafnium cupferronate (Fig. 3) are similar to those for Zr. Zr cupferronates in nitric acid solutions contain less cupferron than Hf cupferronates. This is due to the higher degree of hydrolysis of Zr nitrate and, possibly, to higher electronegativity of Hf. V. S. Syrokomskiy and Yu. V. Klimenko are mentioned. There are 3 figures and 5 tables. The three most important English-language references are: B. Lister, L. McDonald, J. Chem. Soc., 4315 (1952); G. Neumann, G. Lundgren, A. Aurivillius, Acta Chem. Scand. 10, 1670 (1956); P. E. Elving, E. Olson, Analyt. Chem. 26, 1747 (1954); 27, 1817 (1955).

SUBMITTED: July 27, 1961

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S/073/62/028/001/001/004
B110/B138

AUTHORS: Delimarskiy, Yu. K., Sheka, I. A.

TITLE: Present situation and tasks of inorganic chemistry in the Ukraine

PERIODICAL: Ukrainskiy khimicheskiy zhurnal, v. 28, no. 1, 1962, 3-14

TEXT: At the XXII Party Congress of the CPSU it was stated that the increased role of Ukrainian chemistry was due to the establishment of nonferrous and rare metals, fertilizer, nuclear fuel and semiconductors, etc. industries. The 1959 - 1965 plan envisages trebled chemical production, 34 modernized plants, and 30 new ones including Razdol'skoye Sulfur combine, Chernigov Synthetic Fiber combine and others. Superhard and creep resistant alloys, rare and ultrapure metals for nuclear power, the semiconductor and computers industries, ferromagnetics and ferroelectrics are to be given priority. Radiochemical work will be carried out with the nuclear pile designed in the Institut fiziki AN SSR (Institute of Physics AS UkrSSR). Since 1959, the following institutes have been designed: Institut mineral'nykh resursov AN USSR

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(Institute of Mineral Resources UkrSSR) (Simferopol'), Ukrgiprotsvetmet
(Zaporozh'ye), Institut khimicheskikh reaktivov (Institute of Chemical
Reagents) (Donetsk). Others are projected: Institut khimii redkikh
elementov AN USSR (Institute of Element Chemistry AS UkrSSR), Radio-
khimicheskiy institut (Radiochemical Institute), Institut kolloidnoy
khimii AN USSR (Institute of Colloid Chemistry AS UkrSSR). Present
studies are (1) General chemical laws and the development of Mendeleyev's
system. (2) Synthesis and structure of inorganic compounds. (3)
Chemistry of complex compounds and solutions. (4) Chemistry and techno-
logy of rare and nonferrous metals. (5) Physicochemical analysis of
salt and metallic systems. (6) Chemical processing of mineral raw materials.
(1) G. P. Maytak (IONKh AS UkrSSR) has deduced laws regarding the pro-
perties of isotopes and Yu. K. Delimarskiy has worked on the periodic
properties of elektrode potentials. (2) A. I. Brodskiy et al. studied
the synthesis and structure of inorganic compounds, Yu. P. Nazarenko
studied exchange reactions of Cr complexes, G. V. Samsonov examined the
structures of, and developed synthesis for, borides, carbides, silicides,
nitrides, and sulfides of rare earths for refractories and electrical

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engineering, P. G. Aleksandrov also studied rare earth compounds. V. P. Chalym and S. P. Rozhenko developed highly sensitive spinel-type ferro-magnetic materials, E. M. Natanson et al. produced highly disperse metals. (3) A. K. Babko, G. I. Gridchina, and B. I. Nabivanets (IONKh AS UkrSSR) studied Ti and Zr ions in solutions, N. K. Davidenko, V. I. Yermolenko, N. A. Kostromina, Ye. Ye. Kriss, and Z. A. Sheka examined rare earths with salicylic, gluconic, trioxyglutaric acids and tributyl phosphates. Complexes were studied by N. P. Komar', V. N. Tolmachev, and L. P. Adamovich at the Khar'kovskiy universitet (Khar'kov University), by A. M. Golub, F. D. Shevchenko, A. K. Babko, M. M. Tananayko, Ye. G. Zharovskiy, A. T. Pilipenko, and I. V. Pyatnitskiy at the Kiyevskiy uni-versitet (Kiyev University), by A. A. Morozov at the Odesskiy universitet (Odessa University), by A. M. Zharnovskiy in the Gidrometeorologicheskiy institut (Hydrometeorological Institute), and by O. K. Zolotukin, K. N. Mikhalevich, and N. M. Turkevich in L'vov. In Dnepropetrovsk L. M. Volshteyn developed studies on Pt metals by I. I. Chernyayev and A. A. Grinberg. I. G. Ryss (Dnepropetrovsk), L. S. Serdyuk, Yu. I. Usatenko, B Ye. Reznik, I. L. Kukhtevich, N. A. Izmaylov, N. P. Komar', and Ya.

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A. Fialkov worked on complex compounds. (4) Rare-earth elements were
studied by G. M. Shaposhnikov in the Institute of Mineral Raw Materials
AS UkrSSR, by I. V. Vinarov, I. N. Tselik, R. I. Mogunov, A. I. Perfil'-
yev, R. G. Yankelevich in the IONKh AS UkrSSR, by G. V. Samsonov in the
Institut metallokeramiki i spetssplavov AN USSR (Institute of Powder
Metallurgy and Special Alloys AS UkrSSR), by Yu. K. Delimarskiy, I. N.
Sheyko, Ts. V. Pevzner, K. F. Karlysheva, S. A. Kacherova, B. A. Voyto-
vich, B. F. Markov, Ye. B. Gitman, Ye. P. Belyakova, A. A. Shokol, A. D.
Pakhomova, L. F. Kozin, N. S. Fortunatov, D. P. Zosimovich, A. I. Zayats,
and I. F. Frantsevich-Zabludovska in the Institut obshchey i neorgani-
cheskoy khimii (Institute of General and Inorganic Chemistry). A. T.
Nizhnik, V. A. Tsimmergakl together with G. M. Shteyngart and Reznichen-
ko (zavod Elektrotsink (Elektrotsink Plant)) and the Chelyabinskiy
tsinkovoy zavod (Chelyabinsk Zinc Plant) continued studies by Ya. A.
Fialkov and N. V. Akselrud. G. Ya. Gornyy, Ye. S. Burkser, O. A.
Gul'skaya, and N. S. Poluektov worked in the Institut geologicheskikh
nauk AN USSR (Institute of Geological Sciences AS UkrSSR), and N. A.
Tsibrik, M. I. Averchenkov worked in the Institut liteynogo proizvodstva

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AS USSR (Institute of Foundry Work AS UkrSSR). The engineering works in
Kiyev, Khar'kov, Dnepropetrovsk, Zhdanov, Berdyansk, and Riga will use
zirconium supplied by the Samotkanskoye deposit. (5) Physicochemical
studies were conducted by P. P. Budnikov, I. D. Fanchenko, R. V. Chernov,
V. V. Gusev, A. M. Ionizovskiy, and A. T. Chernyy, and also by Ye. M.
Skobets in the IONKh AS UkrSSR, by V. V. Sveshnikov in the Institut
metallo-fiziki AN USSR (Institute of Physics of Metals AS UkrSSR), by
V. N. Yeremenko, and I. N. Frantsevich in the Institute of Powder
Metallurgy and Special Alloys AS UkrSSR, by Ye. Ye. Cherkashin, P. I.
Kripyakevich, Ye. I. Gladyshevskiy, and N. N. Gratsianskiy at the L'vov
gosudarstvennyy universitet (L'vov State University), and also by
scientists of the Fiziko-tekhnicheskiy institut (Physicotechnical Insti-
tute). (6) The processing of raw materials was studied by V. A. Atrc-
shchenko in the Khar'kovskiy politekhnicheskiy Insitut (Khar'kov Poly-
technic Institute), by A. S. Plygunov, A. A. Alent'yev in the Kiyevskiy
politekhnicheskiy institut (Kiyev Polytechnic Institute), Y. A. Berkman
in the L'vovskiy politekhnicheskiy institut (L'vov Polytechnic Institute),
by A. S. Berezhnyy in the Khar'kovskiy institut ogneuporov (Khar'kov

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Institute of Refractory Materials), by B. A. Shoykhet, E. M. Karasik, A. Ye. Sologubenko (MgO production from Sivash brine solution), and D. Ia. Yevdokimov (Odessa) in the Yevpatoriyskaya laboratoriya GIPKh (Yevpatoriya Salt Laboratory GIPKh), by Ya. F. Mezhennyy at the Ukrainskaya sel'skokhozyaystvennaya akademiya (Ukrainian Agricultural Academy), by F. D. Ovcharenko, and also by L. A. Kul'skiy, I. T. Goronovskiy, A. M. Koganovskiy, and M. A. Shevchenko in the IONKh AS UkrSSR. Studies by Ya. A. Fialkov and S. D. Shargorodskiy are being continued.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii AN USSR
             (Institute of General and Inorganic Chemistry AS UkrSSR)

SUBMITTED: June 20, 1961

Card 6/6

21.2500 $aL. 1087$

33725
S/073/62/028/001/002/004
B110/B138

AUTHORS: Sheka, I. A.; Kacherova, S. A

TITLE: Compound of hafnium nitrate and tributyl phosphate

PERIODICAL: Ukrainskiy khimicheskiy zhurnal, v. 28, no. 1, 1962. 38 - 42

TEXT: The reaction of hafnium nitrate with tributyl phosphate (TBP) was studied, and the composition of the complex was determined with solutions of different acidities. 10 ml 0.5-molar, 1.0-molar, and 2-molar TBP solutions in benzene, and 10 ml aqueous $3 \cdot 10^{-5}$ moles/liter Hf with some Hf^{181} and different HNO_3 concentrations, left standing for 5 - 6 days were shaken for 15 min, and the organic phase was decanted. Changes in volume of the phases, and the TBP equilibrium concentration were determined from the difference in acidity of initial and equilibrium solutions. A ξ (B) counter was used for the pulse measurement, made on a 5 ml solution. The equilibrium constant of $Hf^{4+} + 4NO_3^- + nTBP \rightleftharpoons Hf(NO_3)_4 \cdot nTBP$ is

$K = [Hf(NO_3)_4 \cdot nTBP]_{org} / \{[Hf^{4+}]_{aq} [NO_3^-]^4 \cdot [TBP]_o^n\}$, the distribution

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Compound of hafnium nitrate...

coefficient $K_d = K [NO_3]^4 \cdot [TBP]^n \cdot [Hf^{4+}]/C_{Hf_{aq}}$, where $C_{Hf_{aq}}$ is the equilibrium concentration of Hf in an aqueous solution. $[Hf^{4+}]/C_{Hf_{aq}}$ in the Hf microquantities used above, is constant at a constant HNO_3 concentration, and K_d in the equilibrium solution depends on the concentration of free TBP in the organic phase. Hence, the number n of TBP molecules in the complex may be calculated from $K_{d_2}/K_{d_1} = [TBP^2/TBP^1]^n$, where K_{d_1} and K_{d_2} are distribution coefficients of Hf at different TBP concentrations in the organic phase. With 1.23 · 1.58 N HNO_3 in the aqueous phase and 0.35-0.75 moles/liter TBP in the benzene phase, approximately 2 TBP molecules correspond to one Hf atom in the complex. This agrees with values determined by G. F. Yegorov, V. V. Fomin, Yu. G. Frolov, and G. A. Yagodin (Ref. 9: Zh. neorg. kh., 5, 1044 (1960)) for higher HNO_3 concentrations. The distribution coefficients were different for solutions of different age due to the slow depolymerization of polymer Hf ions. The

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Compound of hafnium nitrate.

equilibrium concentration of free TBP was calculated according to Z. A. Sheka, Ye. Ye. Kriss (Ref. 11: Zh. neorg. kh., 4, 2205 (1959)) from the equation $[TBP]_0 = C_{TBP} / \{1 + K_0 [A]_B + K_0 K_1 [A]_B^3\}$, where C_{TBP} is the initial TBP concentration, $[A]_B$ is the concentration of undissociated HNO_3 molecules made to react with TBP, $[TBP]_0$ is the equilibrium concentration of free TBP in the organic phase, $K_0 = 0.65$ and $K_1 = 0.04$ are constants of $HNO_3 \cdot TBP$ and $3HNO_3 \cdot TBP$ formation. K_d has logarithmic dependence of K_d on the TBP equilibrium concentration straight line, with a slope of 2.14. A complex with 2 TBP molecules is formed under the conditions mentioned above. In experiments with solutions containing $6.8 \cdot 10^{-2}$ moles/liter Zr salts, $4.3 \cdot 10^{-2}$ moles/liter Hf salts and 0.731 moles/liter TBP, considerable Zr extraction was observed with 3 moles/liter HNO_3 and Hf extraction occurs with 5 - 6 moles/liter HNO_3. The extraction of Zr and Hf increased with the acidity. With >5 moles/liter, Hf was extracted as the solvates: $HNO_3 \cdot TBP$ and $3HNO_3 \cdot TBP$, since in strongly acid solutions the azido complex

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Compound of hafnium nitrate

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(e.g $Hf(NO_3)_4 \cdot 2TBP \cdot nHNO_3$) passes over to the organic phase. There are
2 figures, 2 tables, and 12 references: 5 Soviet and 7 non-Soviet. The
four most recent references to English-language publications read as fol-
lows: D. F. Reppard et al. J. Physic. Chem. 57. 294 (1953); J. R Hetcher,
Ind Engng. Chem., 76, 7038 (1957); A. E. Levit, H Freund, J. Amer Chem.
Soc., 78, 1545 (1956); Hasford. Mc Kay, Trans Faraday Soc., 54. 573
(1958).

ASSOCIATION: Institut obshchey i neorganicheskoy khimii AN USSR (Institute
            of General and Inorganic Chemistry AS UkrSSR)

SUBMITTED: July 30. 1960

Card 4/4

S/073/62/028/001/004/004
B110/B138

AUTHORS: Karlysheva, K., Sheka, I.

TITLE: Fourth Ukrainian Republic Conference on inorganic chemistry

PERIODICAL: Ukrainskiy khimicheskiy zhurnal, v. 28, no. 1, 1962, 125-129

TEXT: The Fourth Ukrainian Republic Conference on inorganic chemistry,
held in Kiyev March 13-16, 1961, was convened by the Otdeleniye khimiches-
kikh i geologicheskikh nauk AN USSR (Department of Chemical and
Geological Sciences AS UkrSSR) and the Institut obshchey i neorganicheskoy
khimii Akademii nauk USSR (Institute of General and Inorganic Chemistry,
Academy of Sciences UkrSSR). It was attended by 300 research workers,
teachers and industrial chemists from towns all over the USSR. 73 reports
were presented, on the structure and properties of inorganic substances,
chemistry of rare elements and chemical processing of mineral raw
materials. They included the following: Yu. K. Delimarskiy and
I. A. Sheka on the present state and tasks of inorganic chemistry in the
Ukraine; V. P. Chalyy on the kinetics and aging mechanism of metal
hydroxides. V. A. Shoykhet, L. D. Tsigoniy and L. Ye. Sologubenko

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Fourth Ukrainian Republic...

(Yevpatoriya) on a technology for producing MgO, Na_2CO_3, bromine, cement, etc from Sivash salt brine; A. K. Babko and N. M. Lukovskaya (Kiyev) on complex formation in solutions; N. S. Poluektov, S. B. Popova, R. A. Vitkun and L. A. Ovchar (Odessa) talked about almost non-volatile compounds formed in a flame; B. N. Laskorin (Moscow) on ion exchange in nonaqueous media; I. Ye. Starik and Yu. A. Barbanel' (Leningrad) on certain mechanisms of chemical interaction which come under the law of mass action; A. Ye. Gurevich on the structure of uranium peroxide compounds; A. I. Brodskiy and I. F. Franchuk on the isotopic exchange method of studying the structure of uranium peroxide; V. A. Luchenok-Burmakina and A. P. Potemskaya (Kiyev) on the interaction of H_2O_2 with BaO_2 and CaO_2;

A. V. Ablov and N. M. Samus' (Kishinev) on dioximes of trivalent cobalt containing the selenocyanate group; V. V. Skopenko (Kiyev) on silver selenocyanate complexes; by N. V. Tolmachev (Khar'kov) on $[Me(NO_3)_n Dp_m]^{9-}$ type complexes; Yu. I. Usatenko and N. P. Fedash (Dnepropetrovsk) on the reaction of Mn with sodium diethyl-dithio carbaminate; I. L. Kukhtevich (Dnepropetrovsk) on pheophytin dissociation; L. M. Volshteyn, M. F. Mogilevkina and G. G. Motyasina (Dnepropetrovsk) on cis-, and trans-

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Fourth Ukrainian Republic...

S/C73/62/028/001/004/004
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diglycine platinum compounds; B. N. Laskorina, A. G. Maurina,
R. A. Sviridova, I. A. Logvinenko, and V. K. Timofeyeva (Moscow) on metal
adsorption by solid (AH-2Ф (AN-2F), ЭАЭ -10П (EDE-10P), AM (AM), AH-1
(AN-1), ИPA -4O (IRA-4O)) and liquid anionites, and AГ-3 (AG-3) activated
charcoal; A. A. Morozov, N. L. Olenovich, V. N. Yermilova (Odessa) on the
distribution coefficient on СГ-1 (SG-1) cationite; B. A. Voytovich,
A. S. Barananova and N. K. Tumanova (Kiyev) on binary systems;
N S. Fortunatov and Z. A. Fokina (Kiyev) on the solubility of metal
chlorides; A. M. Zharnovskiy (Odessa) on bromo and iodo thalliates of
bivalent metals; N. F. Zakhariya, O. P. Turulina and N. A. Fuga (Odessa)
on the reaction mechanism of ZrO_2 and metal oxides in a flame;

L Ya. Yevdokimov (Odessa) on an examination of the combined oxidation of
arsenic compounds by atmospheric oxygen with nitric oxides and nitric acid
on activated charcoal; V. M. Litvinchuk and K. N. Mikhalevich (L'vov) on
the reduction properties of complex hydroxocyanides of quadrivalent
tungsten; A. N. Kuznetsov and N. F. Kulish (Dnepropetrovsk) on the reduc-
tion of iron, cobalt, and nickel oxides; K. N. Potemkina and S. K Grebneva
(Simferopol') on magnetochemical examinations of iron oxide reduction;
O I. Loyagintsev and Yu. S. Lopatto (Moscow) on natural iron hydroxides;
Card

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N M Dombrovskiy (Chernovtsy) on the formation of sodium triphosphate
during thermal dehydration of mono- and disodium phosphates. 27 reports
were given on rare elements. G. A. Yagodin, G. Ye. Kaplan, O. A. Mostova,
S L Moiseyev, L P ...rayeva (Moscow) reported on the extraction of Zr
and Hf by organophos, ... compounds and their mixtures with nitrate solu-
tions; A A. Lastochk.. . A Sheka (Kiyev) on the reaction of potassium
fluozirconate with ca... ...ода in aqueous solutions K. N. Repenko,
I A. Getman and I V ... (Khar'kov) on the stabilization and de-
stabilization of cubic ... of ZrO_2 Further reports were given by
A K Babko and M. I. ...lo (Kiyev) on examinations of the formation
and relative strength ...nd Ti complexes by the metal indicator method;
by A K Babko and G ...china (Kiyev) on dialysis method of studying
the polymerization of ... quadrivalent elements; I V. Vinarova and
A I Orlova (Odessa) ... extraction method of examining rhodanide
complexes; B I Nabiv.. ...iyev) on the state of Ti(IV) in solutions;
L A Nisel'son, V. A. ...yakin (Moscow) on the separation and purifica-
tion of Zr and Hf on t ...s of various liquids; Ye. B. Gitman (Kiyev) on
the equilibrium betwe.. ...llic Ti and its low chlorides in molten alkali
metal chlorides; V I ... ...nova, A. S. Kereychuk, S. A Bartenev and

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B V. Kolychev on staged complex formation; A. V. Stepanov, V. P. Shvedov
and G. F. Nichugovskiy (Leningrad) the electromigration method of studying
complex compounds of rare-earth elements with lactic acid; N. S. Poluektov
and L. I. Kononenko (Odessa) on the spectrophotometric examination of
carbonate complexes of rare-earth elements; Ye. Ye. Kriss, Z. A. Sheka
(Kiyev) on compounds of rare-earth elements with dibutyl phosphate;
N K. Voskresenska, S. I. Berul' (Moscow) on the interaction of cerium,
neodymium, and samarium oxides with molten salts; G P. Aleksandrov,
V S. Tikhonova, Yu, V. Shevchenko (L'vov) on mixed hexadinitro chelates
and hexanitro cobaltates of rare-earth elements and potassium;
I Yorysh (L'vov) on radiographic examination of mixed nickel hexa-
nitrates of the cerium subgroup and potassium; L. S. Serdyuk, G P. Fedorova
on the reaction of yttrium, lanthane and cerium with alizarin S in the
presence of ammonia and amines; P. I. Kripyakevich, Ye I. Gladyshevskiy,
O S. Zarechnyuk, and I. I. Zalutskiy (L'vov) on X-ray structural analysis
of some intermetallic compounds of lanthanides; A. Ya. Potemkin (Moscow)
on the interaction of copper and antimony in germanium; R M. Dranitska,
A A. Morozov, and A. I. Gavril'chenko (Odessa) on the state of Ge(IV) and
As (III, V) in acid solutions, and the conditions of their separation by

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ion exchange chromatography; V. N. Vigdorovich, A. Ya. Nashel'skiy, and
V. Z. Ostrovska (Moscow) on the synthesis of decomposing compounds
possessing semiconducting properties; A. T. Nizhnik and Z. V. Shekhter
(Kiyev) on the effect of certain impurities on the cementation of gallium
by NaHg; L. I. Dubovenko (Kiyev) on oxalate complexes of Ga and In;
L. L. Vereykina and G. V. Samsonov (Kiyev) on the production and properties
of gallium phosphide. 15 reports were given on the chemical processing of
mineral raw materials. Yu. K. Delimarskiy, I. G. Pavlenko and Yu. G. Roms
(Kiyev) on the production of Bi and Pb by electrolysing fused salts
N. S. Fortunatov, B. V. Stepin and M. P. Pestrikova (Kiyev) on the separa-
tion of metal from dust in the form of hydroxides; S. D. Shargorodskiy and
J. I. Shelud'ko (Simferopol') on the production of HCl gas; S. I. Savchuk
(Kiyev) on HCl purification in DDT production; Ye. P. Belyakova (Kiyev) on
the processing of ilmenite concentrate; R. G. Yenkelevich and I. A. Sheka
(Odessa) on the production of V_2O_5; S. V. Gornev, N. A. Levinskaya and
L. I. Tel'nova (Simferopol') on the production of anhydrous $MgCl_2$;

Ya. F. Mezhennyy, M. A. Yermekov, Yu. Yu. Kerch (Kiyev) on the production
of fertilizers from Kaluga K_2SO_4; K. S. Drozdov, A. I. Moyseyenko.

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Fourth Ukrainian Republic...

S/073/62/028/001/004/004
B110/B138

R. I. Arav and A. M. Ponizovskiy (Simferopol') on the utilization of gypsum obtained as a by-product of the desulfatization of Sivash salt brines; B. A. Shoykhet, L. Ye. Sologubenko, and Z. M. Karasik (Yevpatoriya) on borate extraction; M. N. Machulkin and V. M. Markova (Yevpatorija) on manganate melts obtained from pyrolusite; A. G. Lagutina and V. F. Kovtun (Simferopol') on the autoreduction of Kerch iron ores; A. S. Berezhna and R. A. Kordyuk on the kinetics of the reaction between MgO and Fe_3O_4;

J. Ye. Kaplan, A. V. Machinskiy, I. A. Yakubovich, and T. A. Uspenskaya (Moscow) on the detection of zirconium and spodumene concentrates. The fifth conference is planned for 1963.

Card 7/7

KARLYSHEVA, K.F.; SHEKA, I.A.

Composition of zirconium and hafnium cupferronates. Zhur.-
neorg.khim. 7 no.6:1291-1298 Je '62.   (MIRA 15:6)
      (Zirconium compounds) (Hafnium compounds) (Cupferron)

CHAUS, I.S.; SHEKA, I.A.

Reaction of sodium gallate with sodium sulfide and calcium chloride.
Zhur.neorg.khim. 7 no.9:2162-2166 S '62.   (MIRA 15:9)

1.   Institut obshchey i neorganicheskoy khimii AN UKrSSR.
        (Sodium gallate) (Sodium sulfide) (Calcium chloride)

AM4026340   BOOK EXPLOITATION   s/

Sheka, Ivan Arsen'yevich (Doctor of Chemical Sciences); Chaus,
Ivan Stepanovich (Candidate of Chemical Sciences); Mityureva, Tamara
Trifonovna, (Candidate of Chemical Sciences)

Gallium (Galliy) Kiev, Gostekhizdat USSR, 63. 0296 p. illus.,
   biblio. 1,300 copies printed.

TOPIC TAGS: gallium, gallium chemistry, gallium physics, gallium
compounds, gallium production, gallium abundance, gallium oxide,
gallium halide, gallium carbide, gallium metal compounds

PURPOSE AND COVERAGE: This is the first monograph in the Soviet
Union on the chemistry of gallium and describes chemical and physi-
cal properties of inorganic, organic, and complex compounds of gal-
lium, methods of producing these compounds, their uses, and the
physical and chemical constants of gallium and its compounds. The
book is designed for engineering-technical workers in the rare and

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nonferrous metal industry, and for scientific workers in research institutes. It can be used by graduate students, instructors, and students of chemical-technological and higher educational institutions.

TABLE OF CONTENTS [abridged]:

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Methods of gallium production - - 217
Precipitation of gallium - - 259
Catalytic properties of gallium compounds - - 264
Some questions in the analytic chemistry of gallium - - 266
Literature - - 272

SUB CODE: CH, ML   SUBMITTED: 18Oct63   NR REF SOV: 203

OTHER: 527   DATE ACQ: 20Apr64

Card 3/3

SHEKA, I.A.; CHAUS, I.S.

Coprecipitation of gallium with zinc sulfide in an alkaline medium.
Zhur.neorg.khim. 8 no.2:490-494 F '63.   (MIRA 16:5)
                        (Gallium) (Zinc sulfide)

L 17014-63   EWP(q)/EWT(m)/BDS   AFFTC   JD

S/078/63/008/005/017/021

5 4

AUTHOR: Chaus, I. S. and Sheka, I. A.

TITLE: Coprecipitation of gallium iwth SnS_2

PERIODICAL: Zhurnal neorganicheskoy khimii, v. VIII, No. 5, May 1963,
            1270-1275

TEXT: The study was conducted to determine the effects of acidity,
temperature and gallium concentration upon the coprecipatation of gallium and
stannous sulfide, the amount of quadrivalent tin being constant. The authors
found that the greatest coprecipatation occurred with slight acidity, falling
off sharply with an increase in concentration up to 0.15 - 0.17 N HCl, follow-
ing which it remained constant. Coprecipitation inceased with increase in
temperature. There are 6 figures and 1 table.

ASSOCIATION: Institut obshchey i neorganicheskoy Khimii, Academii nauk SSSR
             (Institute for General and Inorganic Chemistry, Academy of
             Sciences USSR)

SUBMITTED: May 7, 1962

Card 1/1

SHEKA, I.A.; CHAUS, I.S.

Zinc amalgam contact deposition of antimony from acid solutions.
Zhur.prikl.khim. 36 no.1:209-212 Ja '63.   (MIRA 16:5)

1. Institut obshchey i neorganicheskoy khimii AN UkrSSR.
                  (Electroplating) (Antimony) (Amalgams)

SHEKA, Ivan Arsen'yevich,   im. nauk; CHAUS, Ivan
    Stepanovich, kan .   . auk; MITYUREVA, Tamara Trifonovna,
    kand. khim. nauk; SAZHIN. V.S., kand. tekhn. nauk,
    retsenzent; RAYTBURD, L.L., inzh., red.izd-va; BEREZOVYY,
    V.N., tekhn. red.

    [Gallium] Gallii.   izdat USSR, 1963. 296 p.
                                        (MIRA 17:1)

SHEKA, I.A.; LASTOCHKINA, A.A.

Interaction of potassium hexafluorohafniate with ammonia and
alkalies. Zhur. neorg. khim. 8 no.10:2295-2301 O '63.
(MIRA 16:10)

1. Institut obshchey i neorganicheskoy khimii AN UkrSSR.
(Hafnium compounds)   (Alkalies)

LAVROVA, G.V.; TSIMMERGAKL, V.A.; SHEKA, I.A.

Polarographic behavior of indium in citric acid solutions.
Ukr.khim.zhur. 29 no.6:604-609 '63.   (MIRA 16:9)

1. Institut obshchey i neorganicheskoy khimii AN UkrSSR.
         (Indium compounds) (Polarography) (Citric acid)

SHEKA, I.A.; LAVROVA, G.V.

Determination of the number of electrons during indium
reduction on a mercury electrode in citric acid solutions.
Ukr. khim. zhur. 29 no.8:819-824 '63.   (MIRA 16:11)

1. Institut obshchey i neorganicheskoy khimii AN UkrSSR.

ACCESSION NR: AP4012436   S/0078/64/009/002/0312/0319

AUTHORS: Sheka, I. A.; Kacherova, S. A.; Malinko, L. A.

TITLE: Compounds of zirconium and hafnium with trichloroacetic acid.

SOURCE: Zhurnal neorg. khim., v. 9, no. 2, 1964, 312-319

TOPIC TAGS: zirconium trichloroacetate, hafnium trichloroacetate, preparation, IR spectrum, thermogram

ABSTRACT: Properties of the reaction products (in HCl and HNO_3 at 70-75C for 30-40 min.) of trichloroacetic acid with zirconium and hafnium were studied. The product $Zr(OH)_2 (CCl_3COO)_2$ is stable on heating to 220C; it starts to decompose at 275C without melting. $Hf(OH)_2 (CCl_3COO)_2$ is similarly formed. A study of the IR spectra of the Zr and Hf trichloroacetates, dioxides and oxychlorides shows that the Zr and Hf trichloroacetates in the solid state retain the $Zr(OH)_2^{2+}$ ions. Orig. art. has: 5 figures, 4 tables and 1 formula.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii AN USSR
          (Institute of General and Inorganic Chemistry AN USSR).

Card 1/1

ZAITSEVA, A.A.; SHEKA, I.A.

Interaction of potassium hexafluorotitanate with sodium hydroxide and ammonia. Ukr. khim. zhur. 30 no.9:896-900 '64.
(MIRA 17:10)

1. Institut obshchey i neorganicheskoy khimii AN UkrSSR.

SAVENKO, N.F.; SHEKA, ...

Reaction of zirconium and hafnium chlorides with potassium fer-
rocyanide in aqueous solutions. Ukr. khim. zhur. 31 no.1:18-23
'65.   (MIRA 18:5)

1. Institut obshchey i neorganicheskoy khimii AN UkrSSR.

LYAKH, O.D.; SHEKA, I.A.; PERFIL'YEV, A.I.

Reaction of germanium dioxide with ammonia and urotropine
in aqueous solutions. Zhur.neorg.khim. 10 no.8:1822-1826
Ag '65.   (MIRA 19:1)

1. Laboratoriya instituta obshchey i neorganicheskoy khimii AN
UkrSSR. Submitted October 8, 1964.

LEBEDEV, O. A.; FRANTAS'YEV, N. A.; OLYUNIN, G. V.; MUZHZHAVLEV, K. D.; SHEKA, V. P.; SHEKA, T. S.

Developing a method of mechanized removal of electrolytic slime in magnesium production. TSvet, met, 36 no. 11:38-41 N '63.   (MIRA 17:1)

L 28970-66   EWT(m)/EWP(e)/T/EWP(t)/ETI   IJP(c)   DS/JD/WW/WH

AUTHOR: Muzhzhavlev, K. D.; Lebedev, O. A.; Frantas'yev, N. A.; Olyunin, G. V.;
Dolgikh, T. K.; Sheka, T. S.

ORG: none

TITLE: Improvement in the technology of magnesium chloride electrolysis

SOURCE: Tsvetnyye metally, no. 3, 1965, 60-65

TOPIC TAGS: electrolyte, electrolysis, titanium, magnesium, chloride, furnace, magnesium compound, chlorination

ABSTRACT: On the basis of the pilot plant investigations conducted by the authors in 1959-1960, a sodium-potassium electrolyte composed of (%):8-18 $MgCl_2$, 60-30 NaCl, 20-50 KCl, 0-10 $CaCl_2$ or $BaCl_2$, was recommended for the electrolysis of $MgCl_2$ obtained from the production of titanium.

In 1961-1963, at one magnesium plant, extensive research of the sodium - potassium electrolyte was conducted at a group of experimental industrial electrolyzers operated for 1-1.5 years after replacement of the lining before the beginning of the tests. For comparison, the sodium-calcium and potassium electrolytes were tested simultaneously under comparable conditions.

The electrolyzers were fed molten $MgCl_2$ from titanium production containing (%): 95-99 $MgCl_2$, 0.4 MgO, 0.004 SiO_2, 0.007 Fe, $\angle$ 0.02 C, 0.01 SO_4^{-2}, 0.01 F^-, 0.04 H_2O, and 0-2 Mg metal.

The slime from the electrolyzers was removed manually once in 7 days; the distance between electrodes was kept at 8-10 cm; fluorides were not introduced into the electrolyzers. The anode current density for all electrolyzers was identical - 0.43 a/cm^2. In contrast to the earlier issued recommendations, the electrolyte temperature was kept at 700-720°C.

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L 28970-66

ACC NR: AP6019136

        To control the true value of the current yield the electrolyzers were
periodically (6-10 days) changed to a feed of $MgCl_2$ obtained in electrical
shaft furnaces.

        Identically high and stable average current yield, approximating 90%,
was obtained in the sodium-potassium and potassium electrolyzers. The
current yield for the sodium-calcium electrolyte was 4-6% lower.

        The amount of slime in the potassium and sodium-potassium electrolytes
was identical (0.06 kg/mg Mg); in the sodium-calcium electrolyte, 70% more
slime was obtained.

        Because of these factors the actual electrical conductivity of the
sodium-potassium electrolyte is approximately 20% higher than the electrical
conductivity of the sodium-calcium electrolyte with the same amount of NaCl
in the electrolyte.

        The amount of magnesium raw material in the main impurities, the losses
of metallic magnesium with the slime, the yield and concentration of chlorine,
and the stability of the lining in the experimental industrial electrolyzers
were identical for all three electrolyte compositions.

        Relationship of current yield to the interelectrode distance showed in
pilot-plant electrolyzers of the All-Union Aluminum and Magnesium Institute
(VAMI), that the change in distance between electrodes within the limits of
3-16 cm does not at all affect current yield.

        In 1963, this relationship was studied on an experimental industrial
electrolyzer. When the composition of the electrolyte was (in %): 8-12 $MgCl_2$,
22-24 NaCl, 63-56 KCl and 3.0 $CaCl_2$, the current yield and the electric

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L 28970-66

ACC NR: AP6019136   0

power consumption remained almost unchanged upon decreasing the interelectrode distance from 8-9 to 4-5 cm, but the current at the electrolyzer cell in the second case was increased by 20% because of the additional current feed from the auxiliary generator and disconnection of one cell. The losses of chlorine with the gases of the cathode suction and its concentration in the anode gas remained unchanged. The amount of slime also remained unchanged.

Relationship of current yield and slime content to the $MgCl_2$ concentration in the electrolyte was conducted on the pilot plant electrolyzer of VAMI at 2000 amps.

Granulated $MgCl_2$ from titanium production containing (in %): 0.5-1.5 H_2O, 0.4-0.7 MgO was the raw material. $MgCl_2$ was loaded into the electrolyzer continuously with the aid of a trough feeder. The variation in concentration in a single period did not exceed 1%, and the electrolyte level was kept strictly constant.

If one takes, as 100%, the amount of slime when the concentration of $MgCl_2$ is 6%, then when the content of $MgCl_2$ in the electrolyte is 9, 13 and 16%, this value is 118, 154, and 195% respectively. Increased $MgCl_2$ concentrations in the electrolyte from 6-9 to 13% led to the increase of current yield from 86 to 90%.

It is evident that to obtain a high and stable current yield the $MgCl_2$ concentration in the electrolyte of industrial electrolysers should not be below 8-10% (the upper limit -- not over 18-20%)

It is interesting to note that the $MgCl_2$ content change in the range of 6-16% in the electrolyte did not at all affect the value of the average

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voltage of the electrolyzer.

The cause of this, evidently, is the fact that the reverse emf measured by the instantaneous cut-out of a cell was 2.92 V at 6% $MgCl_2$ and 2.28 V at 16% $MgCl_2$.

Relationship of the current yield and slime content to the duration of intervals between recoveries of slime at the VAMI pilot plant electrolyzer showed that the duration of interval between extraction of the slime was increased to 142 days; thereupon the amount of slime amounted to 0.01 kg/kg Mg in all.

In 1961, in an experimental industrial electrolyzer, the time of the intervals between slime removal was set at 40-50 days; the current yield was 85-87%. In 1963 this task was studied more in detail at two experimental industrial electrolyzers.

From the data obtained it follows that when feeding $MgCl_2$ from titanium production to electrolyzers the slime content depends not so much on the amount of raw material, composition of the electrolyte and design of the electrolyzer as on the conditions for slime recovery.

Testing of an electrolyzer with a graphite hearth with $MgCl_2$ feed from the titanium production was conducted on pilot plant scale for 4 months.

The total current at the electrolyzer was 2000 amps; the current shunted to the hearth -- 100-200 amps (D = 0.03-0.06 amps/cm^2).

With a disconnected hearth, the current yield and slime formation were the same as in the pilot plant electrolyzer with an ordinary hearth.

During anode polarization of the graphite hearth, the slime completely

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disappeared in 2-3 days; during operation with a connected hearth no slime
was formed.

However, both in the first and also in the second case the current
yield was reduced from 88-91 tp 80-85%, i.e., by 5-8%. This can be explained
by the chlorination of impurities and their harmful effect on the process.
Research in this area will be continued. Of much interest in remo ing the
harmful effect of impurities is the use of chlorine-discharging anodes with
which all or part of the chlorine is carried off through the body of the anode.
Such experiments are being conducted at the present time.

With the further mastery of the sodium-potassium electrolyte, increase
of NaCl in it, and the introduction into industry of the operating regimes
at small distances (4-5 mm) between electrodes, these indicators in the
opinion of the authors, can amount to 88-90% and 50.4-52.2 megajoules/kg of
Mg (14.0-14.5 kilowatt-hours/kg of Mg) respectively, when the current is
20-30% higher than at the present.

The tests on experimental industrial electrolyzers, as well as the
physical and chemical properties of the sodium-potassium electrolyte which
are favorable to the electrolytic process and the high quality of $MgCl_2$ from
the production of titanium, can serve to conform this.

The selection of the actual ratio of NaCl:KCl in the electrolyte depends
on the technical scheme of the plant and level of mechanization of slime
recovery processes. As the calculation of economic effectiveness indicates,
the use of the sodium-potassium electrolyte in place of the sodium-calcium one
permits a reduction of approximately 5% in the cost of magnesium.

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ACC NR: AP6019136

0

Additionally, the use of this electrolyte permits the mechanisation of the slime recovery with the aid of a vacuum. With sodium-calcium or sodium-barium electrolytes this means of slime recovery is hardly applicable because of the large losses of $CaCl_2$ or $BaCl_2$. The sodium-potassium electrolyte should be recommended for use, in turn, for high quality $MgCl_2$. However, in the future this electrolyte composition may be quite practical for all forms of $MgCl_2$. Orig. art. has: 5 tables. [JPRS]

SUB CODE: 13, 07 / SUBM DATE: none / ORIG REF: 006

Card 6/6   BLG

MUZHZHAVLEV, K.D.; LEBEDEV, O.A.; FRANTAS'YEV, N.A.; OLYUNIN, G.V.;
     SHEKA. T.S.; FOLGIKH, T.K.; Prinimali uchastiye: POPOV, V.V.;
SHEKA, V.P.

Results of testing individual design elements of magnesium
electrolytic cells. TSvet. met. 38 no.5:57-60 My '65.
                                                          (MIRA 18:6)

81640
S/181/60/002/06/28/050
B006/B056

24.4500

AUTHOR: Sheka, V. I.

TITLE: The Symmetry of the Energy Bands of an Electron With Spin

PERIODICAL: Fizika tverdogo tela, 1960, Vol. 2, No. 6, pp. 1211-1219

TEXT: In the present paper, the author investigates the structure of
the energy bands of a Dirac electron by employing group-theoretical
methods. Group-theoretical investigations of the energy-band structure
of crystals in consideration of spin-orbit interaction have repeatedly
been carried out. In these papers, an additional symmetry with respect
to time reversal was taken into account when determining the dispersion
laws in the case of a concrete selection of the basic functions of the
irreducible representations of the space group. E. I. Rashba (Ref. 7),
however, showed that the energy band structure cannot depend on a spe-
cial selection of the form of irreducible space-group representation,
but is determined only by the character of these representations.
In the present paper, the author solves the problem of determining the
points with zero inclination on the energy surfaces $E(\vec{k})$ in

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Electron With Spin

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consideration of the time reversal for a Dirac electron in an arbitrary crystal field. After derivation of the formulas for determining these points, the dispersion law is determined with an accuracy up to terms of the order of K^2. The results of the theory are then applied to crystals with zinc-blende symmetry (point space group T_d^2), in which case the denotation was taken from Ref. 2. The author finally thanks E. I. Rashba for supervising the investigation. There are 14 references: 6 Soviet, 6 American, 1 German, and 1 British.

ASSOCIATION: Institut fiziki AN USSR, Kiyev (Institute of Physics of the AS UkrSSR, Kiyev)

SUBMITTED: July 6, 1959

Card 2/2

24915   S/181/61/003/006/012/031
                    B102/B201

9,4300

AUTHORS: Rashba, E.I. and Sheka. V.I.

TITLE: Combined resonance of band electrons in crystals with
             zincblende type lattice

PERIODICAL: Fizika tverdogo tela, v. 3, no. 6, 1961. 1735-174?

TEXT: A report on the subject mentioned in the title was delivered at the
Fourth All-Union Conference on Semiconductor Theory, which took place at
Tbilisi on October 22, 1960. The present study is in continuation of a
paper by Rashba (Ref.1: FTT, II, 1224, 1960), where it had been shown that
the existence of spin-orbit interaction may lead to the possible appearance
of a new type of band electron resonance, which can be jointly caused by
the electron vector of the h-f field and a change of electron spin levels.
It is thus designated as combined resonance which may arise in semicon-
ductors with extremum loops (cf. Ref.2: Rashba, Sheka, FTT II, 2,162,
1959). A theory of the combined resonance of band electrons is developed
here for crystals with zincblende-type lattice, and the angular dependence
of resonance is calculated. The results point to a marked anisotropy of

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Combined resonance of band ...

the intensity of the resonance effect. The frequencies of the combined resonance prove to be linear combinations of the spin resonance frequency and of the cyclotron resonance. It should be possible to estimate the extent of band splitting (which is related to the absence of an inversion center) from measurements of the intensity of the combined resonance. Crystals with inversion center display a twofold degeneracy of the bands in the entire $\vec{k}$-space, while crystals without an inversion center display no such band degeneracy. In the latter crystals, however, there appears, e.g., near the center of the Brillouin zone a small but finite band "divergence" (caused by spin-orbit interaction) which is hardly measurable. In the authors' opinion, a study of the combined resonance would make it possible to find a usable method of measuring the parameters of the relativistic band divergence. The crystals considered here (e.g., InSb, ZnS) belong to the space group T_d^2. The Hamiltonian is first determined and examined for the system concerned. It is put in the form $H = H_0 + H_1$, where

$H_0 = A\hat{k}^2 + \frac{g\beta_0}{2}(\vec{\epsilon}\vec{x})$, and $H_1 = \delta_0(\vec{\epsilon}\hat{k})$; $A = \hbar/2m^*$, m^* is the effective mass,

$\delta_c = e\hbar/2m_0c$, m_0 is the mass of the free electron; $\vec{\epsilon}$ is the Pauli matrix,

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ξ_0 is the parameter characterizing the band divergence; $\hat{\kappa} = \hat{k}_y \hat{k}_x \hat{k}_y$ $- \hat{k}_z \hat{k}_x \hat{k}_z$ (the other components have to be obtained by cyclic permutation). The operator of the quasimomentum is related to the vector potential in the usual manner: $\hat{k} = -i \nabla + e\vec{A}/c$. The further investigation is restricted to small ξ_0, so that H_1 may be regarded as a perturbation. The absorption in the antinode of the electric field is described by the imaginary part $\varepsilon''(\omega)$, and by $\mu''(\omega)$ in the antinode of the magnetic field. Formulations for the matrix elements of the transition are examined next; the magnetic field is designated by the polar angle θ and the azimuth Φ; representation

$$S = \left\| \begin{matrix} \alpha & \beta \\ \gamma & \delta \end{matrix} \right\| = \left\| \begin{matrix} \cos\frac{\theta}{2}\exp\left[\frac{i}{2}\left(\frac{\pi}{2}+\Phi\right)\right] & \sin\frac{\theta}{2}\exp\left[\frac{i}{2}\left(\frac{\pi}{2}-\Phi\right)\right] \\ -\sin\frac{\theta}{2}\exp\left[\frac{i}{2}\left(\Phi-\frac{\pi}{2}\right)\right] & \cos\frac{\theta}{2}\exp\left[-\frac{i}{2}\left(\frac{\pi}{2}+\Phi\right)\right] \end{matrix} \right\| . \quad (18)$$

is used.

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$$\sqrt{2}\,\frac{\tau_0 m^*}{\hbar^2}\,\frac{e\mathcal{H}}{ch}\,\frac{q_2}{j-l-q_a+\beta^*}\sum_{\beta\gamma}B_{(a\beta\gamma)}\langle l|\,a_\beta a_\gamma\,|j\rangle.$$

(30) is obtained for the matrix element, and

$$\langle l-|V_a|j+\rangle=\sqrt{2}\,\frac{\tau_0}{\hbar}\,\frac{e\mathcal{H}}{ch}\,\frac{l-j-\beta^*}{l-j+q_a-\beta^*}\sum_{\beta\gamma}B_{(a\beta\gamma)}\langle l|a_\beta a_\gamma|j\rangle. \qquad (31)$$

for the angular dependence of the resonance effect. The unitary B-matrix
is given by

$$B=\begin{vmatrix} -\dfrac{1}{\sqrt{2}}(\sin\Phi+i\cos\theta\cos\Phi) & -\dfrac{1}{\sqrt{2}}(\sin\Phi-i\cos\theta\cos\Phi) & \sin\theta\cos\Phi \\[2mm] \dfrac{1}{\sqrt{2}}(\cos\Phi-i\cos\theta\sin\Phi) & \dfrac{1}{\sqrt{2}}(\cos\Phi+i\cos\theta\sin\Phi) & \sin\theta\sin\Phi \\[2mm] \dfrac{i}{\sqrt{2}}\sin\theta & -\dfrac{i}{\sqrt{2}}\sin\theta & \cos\theta \end{vmatrix}. \qquad (20)$$

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its elements are explicitly given by

$$B_{(111)} = 0,$$

$$B_{(133)} = -2B_{(113)} = \frac{2}{3}B_{(222)}^{\cdot} = \cdot$$

$$= \cos 2\Phi \cos 2\theta - \frac{i}{2} \sin 2\Phi \cos \theta (2\cos^2 \theta - \sin^2 \theta),$$

$$B_{(122)} = -\frac{1}{2}B_{(233)} = \frac{3}{4} i \sin 2\Phi \sin \theta \sin 2\theta,$$

$$B_{(333)} = -2B_{(123)} = \frac{6}{5}B_{(223)}^{\cdot} =$$

$$= \frac{3i}{2\sqrt{2}} [\cos 2\Phi \sin 2\theta - i \sin 2\Phi \sin \theta (2\cos^2 \theta - \sin^2 \theta)],$$

$$B_{(113)} = \frac{3}{4\sqrt{2}} [\sin 2\Phi \sin \theta (1 + \cos^2 \theta) + i \cos 2\Phi \sin 2\theta].$$

$$(32)$$

for the case concerned. As may be seen from (31), transitions with a change of the orbital quantum number by 0, ±1, and ±2 are possible in the combined resonance. Using (31), the angular diagrams of combined resonance.

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are then examined. For the individual perturbation operators, the distribution of the various transitions in the combined resonance according to the types of angular diagrams is represented as follows:

	v_+		v_-		v_z	
	$+\rightarrow-$	$-\rightarrow+$	$+\rightarrow-$	$-\rightarrow+$	$+\rightarrow-$	$-\rightarrow+$
I	$i\rightarrow i-2$			$i\rightarrow i+2$		
II	$i\rightarrow i$	$i\rightarrow i\pm2$	$i\rightarrow i\pm2$	$i\rightarrow i$	$i\rightarrow i-1$	$i\rightarrow i+1$
III	$i\rightarrow i+2$	$i\rightarrow i$	$i\rightarrow i$	$i\rightarrow i-2$	$i\rightarrow i+1$	$i\rightarrow i-1$
IV	$i\rightarrow i+1$	$i\rightarrow i\pm1$	$i\rightarrow i\pm1$	$i\rightarrow i-1$	$i\rightarrow i,i+2$	$i\rightarrow i,i-2$
V	$i\rightarrow i-1$			$i\rightarrow i+1$	$i\rightarrow i-2$	$i\rightarrow i+2$

Finally, the intensity of the combined resonance is examined, namely, 1, for a nondegenerate electron gas, 2, for a degenerate one of low concentration, and 3, for a degenerate one of high concentration. The criteria for the application of this theory are finally discussed briefly. There are 1 table and 8 references: 4 Soviet-bloc and 4 non-Soviet-bloc.

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                                             B102/B201

ASSOCIATION: Institut poluprovodnikov AN USSR Kiyev (Institute of
               Semiconductors. AS UkrSSR, Kiyev)

SUBMITTED: December 29, 1960

Card 7/7

24930   S/181/61/003/006/027/031
                     B102/B214

9,4300

AUTHORS: Rashba, E. I. and Sheka, V. I.

TITLE: Combined resonance in n-type InSb

PERIODICAL: Fizika tverdogo tela, v. 3, no. 6, 1961, 1863 - 1870

TEXT: The present paper formed the subject of a lecture delivered on
October 22, 1960 at the Fourth All Union Conference on Semiconductor
Theory held at Tbilisi. The paper is in continuation of an earlier
paper (Ref. 1: FTT, III, 6, 1732, 1961) in which a report was given on
the investigations of the combined resonance of the band carriers in
crystals having zinc blende type of lattice. There it was assumed that
the extremum of the band is reached at $\vec{k} = 0$. This, for example, is the
case in n-type InSb to which the results of Ref. 1 are applied with a
view particularly to estimating the intensity of the combined resonance
in this lattice. First, the Hamiltonian of the band electrons and the
determination of various constants are discussed. Next, the intensities
of the combined resonance and the paramagnetic resonance are compared.
Fig. 2 shows the scheme of the electron transitions in InSb for the

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combined resonance (A), the cyclotron resonance (B), and the paramagnetic resonance (C). The distance between the nearest levels with opposite quantum numbers σ is $1/\beta^* = 2m_0/gm^*$ times smaller than the distance between the Landau levels. The ratio of the intensities of combined and paramagnetic resonance is determined by the formula $\eta^{-1}(\alpha,\sigma,\Delta j,\zeta) = \dfrac{\varepsilon_\alpha''(\omega_{c.res.})}{\varepsilon'\mu''\varepsilon(\omega_{p.res.})}$.

In InSb, $m^*/m_0 = 0.013$, $\beta^* = -0.33$, $\varepsilon' = 17$, and $L = \dfrac{8}{\varepsilon^r}\left(\dfrac{\delta_0 m_s m^* c}{\hbar^3}\right)^2 \approx 10^2$.

The following special cases are now investigated: 1)Nondegenerate electron gas. a) High temperature, $\lambda \ll 1$

$$\eta_h(\sigma, \Delta j) = \frac{\Gamma\left(\frac{5}{2} - \Delta j\right)}{\sqrt{\pi}} \frac{1 + \delta_{0,\,2-\Delta j}}{\lambda^2} \left| \frac{\Delta j - \sigma \beta^*}{\beta^*} \right|. \tag{11}$$

holds. The intensity of the combined resonance is always substantially higher than that of the paramagnetic resonance. b) Low temperature, $\lambda \gg 1$. The intensity ratio is given by

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$$\eta_1(\sigma, \Delta j) = \frac{\Gamma\left(\frac{5}{2} - \Delta j\right)}{\sqrt{\pi}\lambda^{2-\Delta j}} \left(\delta_{1,\sigma} + \delta_{1,-\sigma} e^{-\lambda|\beta^*|}\right) \sum_{r=0}^{\Delta j} a_r \left(\frac{1}{2}\right)^r + \frac{9}{16}\delta_{0,\Delta j}. \quad (12)$$

For $\Delta j = 0$, $\eta^{-1}(\sigma,0) = 9/16$, i. e. the combined resonance exceeds the paramagnetic resonance 28, 10, and 125 times for α values, 1, 2, , and 3. For $\Delta j = 2$ and $\sigma = 1$, $\eta^{-1}(1,2) = 310$, 330, and 230. In the remaining cases the combined resonance is weaker than the paramagnetic one when λ is not too small. 2) Degenerate electron gas. Low concentration. One has

$$\eta_1(\sigma, \Delta j, N) = \frac{2^{2-\Delta j}}{5 - 2\Delta j}\left(\frac{\pi^2 N}{k_\chi^3}\right)^{2(2-\Delta j)} \sum_{r=0}^{\Delta j} a_r \left(-\frac{1}{2}\right)^r +$$

$$+ \delta_{0,\Delta j}\left\{-\frac{1}{3}\left(\frac{\pi^2 N}{k_\chi^3}\right)^2 + \frac{1}{16}\right\}, \qquad (13)$$

It is found (notations as above) that $\eta^{-1}(1,0) = 3$, 1, and 14; $\eta^{-1}(1,2) = 100$, 110, and 78; $\eta^{-1}(-1,2) = 154$, 0, and 34. 3) Degenerate electron gas. High concentration. One has

$$\eta_1(\sigma, \Delta j, \zeta) = \frac{4}{15\sqrt{\pi}}\Gamma\left(\frac{5}{2} - \Delta j\right)(1 + \delta_{0, 2-\Delta j})\left|\frac{\Delta j - \sigma\beta^*}{\beta^*}\right|\zeta^2. \qquad (14)$$

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                                                                      B102/B214

The intensity of the combined resonance is always higher than that of
the paramagnetic resonance. The table gives the intensity ratios for a
degenerate electron gas' for maximum values of the coefficients $B(\alpha, \sigma, \Delta j)$.
Finally, the results are briefly discussed and compared with those of
Bemski. The authors thank K. B. Tolpygo for discussions.   There are
3 figures, 2 tables, and 9 references: 2 Soviet-bloc and 7 non-Soviet-
bloc. The most important references to English-language publications
read as follows: L. M. Roth, B. Lax, S. Zwerdling. Phys. Rev., 114, 90,
1959; H. Welker, H. Weiss, Solid State Physics, 3, 1, 1956; G. Bemski,
Phys. Rev. Lett., 4, 62, 1960.

Table

α	σ				
	1	1	1	−1	−1
	Δj				
	2	1	0	2	1
1	·190	950	9.8	210	120
2	210	55	3.4	0.00	5.7
3	150	290	45	46	110

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27290

S/181/61/003/008/020/034
B102/B202

24.7700 (1138, 1144, 1160)

AUTHORS: Rashba, E. I. and Sheka, V. I.

TITLE: Properties of semiconductors with extremum loops.
IV. Angular dependence of combined resonance in a strong
magnetic field

PERIODICAL: Fizika tverdogo tela, v. 3, no. 8, 1961, 2369-2376

TEXT: The author devised a theory of combined resonance in semiconductors
with extremum loops in a strong magnetic field in order to determine the
angular dependence of the resonance intensity. If the depth Δ of the loop
is sufficiently large and if the characteristic energy of the electrons
contributing to the various effects is lower than Δ or of the same order of
magnitude, a large number of methods exists for determining the existence
of an extremum loop and also for determining Δ (cyclotron resonance,
magnetic susceptibility, galvanomagnetic effect, optical properties etc.)
if $\Delta \ll E_{char}$. However, only one method can be applied: Study of combined
resonance which has been predicted by Rashba. In strong magnetic fields

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S/181/61/003/008/020/034
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spin-orbit coupling is destroyed if the Zeeman energy is considerably higher than the spin-orbit separation of the bands in the effective region of the k space; with spin resonant frequency an absorption which is induced by the electric vector of the h-f field occurs simultaneously with paramagnetic resonance. This resonance is designated as combined resonance. Its intensity is by orders of magnitude higher than that of paramagnetic resonance and may come close to that of cyclotron resonance. Δ can be directly determined from its intensity. The authors now determine the angular dependence of combined resonance by a method that had been devised in a previous paper (FTT, III, 1735, 1961). The designations are taken from this previous paper and from Ref. 3 (Rashba, FTT, II, 1224, 1960) [Abstracter's note: For this reason, the author omits the formulas obtained. In order to be able to follow the theoretical considerations the mentioned previous papers should be known]. If the Zeeman energy is very high compared with the characteristic band separation Δ_{char} combined resonance can be observed if $h\nu > \Delta$, where ν is the frequency of the electromagnetic wave. With $\nu \sim 10^{11}$ cps semiconductors with $\Delta \leq 10^{-5}$ ev can be studied. The shift of the ceiling of the valence band from $k = 0$ by 10^{-4} ev

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B102/B202

for InSb brings out the importance of this range of values. In crystals consisting of light elements Δ may be considerably smaller. If ν is in- creased by transition into the far infrared, the Δ range can be extended. In crystals with large g factor ν can be strongly increased without ex- tension beyond the range of practically attainable magnetic fields. In n-type InSb, where the extremum is not shifted from k = 0, the spin-orbit coupling may be destroyed and the limiting case of combined resonance can be observed at any frequency ν if the carrier concentrations and the temperatures are sufficiently low. A limitation is given only by the finiteness of the relaxation time. The intensity ratio of combined and cyclotron resonance is of the order of $\sim \Delta/E_{char}$ for $\Delta_{char} \leqslant h$. There are 12 references, 9 Soviet-bloc and 3 non-Soviet-bloc. The three references to English-language publications read as follows: R. C. Casella. Phys. Rev. Lett., 5, 371, 1960; W. Shockley. Phys. Rev. 90, 491, 1953; S. J. Czyzak et al. J. Opt. Soc. A, 47, 240, 1957.

ASSOCIATION: Institut poluprovodnikov AN USSR Kiyev (Institute of Semi-
conductors AS UkrSSR, Kiyev)

Card 3/4

PEKAR, S. I.; RASHBA, E. I.; SHEKA, V. I.

"Combined resonance on impurity centers and in inhomogeneous magnetic fields."

report submitted for Intl Conf on Physics of Semiconductors, Paris, 19-24 Jul 64.

S/0181/64/006/001/0141/0152

ACCESSION NR: AP4011751

AUTHORS: Rashba, E. I.; Sheka, V. I.

TITLE: Combination resonance at local centers of large radius

SOURCE: Fizika tverdogo tela, v. 6, no. 1, 1964, 141-152

TOPIC TAGS: combination, combination resonance, band carrier, band electron, transverse resonance, longitudinal resonance

ABSTRACT: The authors have developed a theory on combination resonance at large-radius donor centers. They note that the conditions for combination resonance to arise are not as favorable under these circumstances as for band electrons. Combination resonance is excited by the electron vector of electromagnetic waves and is therefore proportional to the square of the radius of the electron orbit. The authors have shown that combination resonance must be observed in transverse circular polarization and in longitudinal polarization. The resonance intensity depends markedly on the angle between the steady uniform magnetic field and the symmetry axis. In this, the angular dependence coincides with the value obtained by E. I. Rashba and V. I. Sheka (FTT, 3, 2369, 1961) for band carriers. Two cases

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ACCESSION NR: AP4011751

were considered: for transverse resonance and for longitudinal resonance. It was found that transverse resonance for $g > 0$ is markedly different from transverse resonance with $g < 0$ and from longitudinal resonance. In the first ($g > 0$), resonance intensity is limited, but in the other two the magnetic field becomes infinite. Orig. art. has: 4 figures and 45 formulas.

ASSOCIATION: Institut poluprovodnikov AN UkrSSR,Kiyev (Institute of Semiconductors, AN UkrSSR)

SUBMITTED: 17Jul63   DATE ACQ: 14Feb64   ENCL: 00

SUB CODE: PH   NO REF SOV: 007   OTHER: 008

. Card 2/2

ACCESSION NR: AP4013524

AUTHORS: Rashba, E. I.; Shek., . I.

TITLE: The theory of combination resonance at acceptor centers

SOURCE: Fizika tverdogo tela, v. 6, no. 2, 1964, 576-583

TOPIC TAGS: combination resonance, indium antimonide, spin orbit splitting, deformed crystal, acceptor center

ABSTRACT: This article is a continuation of previous work by the authors (FTT, 6, 141, 1964), in which they analyzed the factors affecting intensity of combination resonance at local centers of large radius. In the present paper they determine the intensity values and derive angular diagrams for combination resonance at acceptors in crystals of InSb. Large spin orbit splitting of the hole band and the absence of an inversion center, characteristic of these crystals, must lead to high intensity of combination resonance. The angular diagrams indicate marked anisotropy of the resonance. A Hamiltonian is set up, and it is found that, at parameter values corresponding to InSb, combination resonance is determined chiefly by the nonrelativistic cubic members of the Hamiltonian. Determination of the intensity

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ACCESSION NR: AP4013524

shows that in undeformed samples this intensity must exceed the intensity of paramagnetic resonance approximately by the sixth order. Therefore, high intensity of combination resonance in deformed samples should also be expected. "We thank G. Ye. Pikus and G. L. Bir for valuable discussions and for furnishing a preprint of the article of G. L. Bir, Ye. I. Butikov, and G. Ye. Pikus (Phys. Chem. Sol. 25, no. 12, 1963)." Orig. art. has: 20 formulas.

ASSOCIATION: Institut poluprovodnikov AN UkrSSR,Kiev(Institute of Semiconductors AN UkrSSR)

SUBMITTED: 18Sep63   DATE ACQ: 03Mar64

SUB CODE: EC, SS   NO REF SOV: 009   ENCL: 00

OTHER: 006

Card 2/2

L 11262-65   EWT(1)/EWG(k)/T   Pz-6   IJP(c)/ASD(a)-5/ESD(gs)/ESD(t).   AT

S/0181/64/006/010/3099/3106

ACCESSION NR: AP404667

AUTHOR: Sheka, V. I.

TITLE: Intensity of combined electron resonance in semiconductors with a narrow forbidden band

SOURCE: Fizika tverdogo tela, v. 6, no. 10, 1964, 3099-3106

TOPIC TAGS: electron resonance, forbidden band, resonance band, conduction band, valence band, paramagnetic absorption

ABSTRACT: This is a continuation of earlier work by the author (with E. I. Rashba, FTT, v. 3, 1735 and 1863, 1961), devoted to crystals having zinc-blende symmetry. The present investigation is devoted to the singularities in the occurrence of combined reso-nances of electrons, which is due to the non-quadratic nature of the energy E(k) in semiconductors having an InSb band structure. The small width of the forbidden band in such crystals increases

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ACCESSION NR: AP4046627

the role played in the excitation of the combined resonance by the dependence of the g-factor on the quasimomentum. This circumstance leads to the appearance of an isotropic term in the intensity of the two combined-resonance bands (of which one coincides in frequency and in polarization with the paramagnetic absorption band), along with an anisotropic part due to the spin-orbit separation of the bands. The theory developed makes use essentially of a direct account of the interaction between the conduction band and the nearest valence bands; the higher bands introduce small corrections without qualitatively changing the effect. In the approximation considered here, the isotropic part of the intensity of the combined resonance is determined by the parameters of the band structure, which are well known for several semiconductor compounds of the type $A_{III} B_V$; in these crystals the combined absorption exceeds the paramagnetic absorption. "The author thanks E. I. Rashba for suggesting the topic and for continuous interest in the work." Orig.

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art. has: 1 figure, 19 formulas, and 2 tables.

ASSOCIATION: Institut poluprovodnikov AN UkrSSR, Kiev (Institute of Semiconductors, AN UkrSSR)

SUBMITTED: 11May64

SUB CODE: SS   NR REF SOV: 005

ENCL: 00

OTHER: 006

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L 2295-66   EWT(1)/T/EWA(h)   IJP(c)   A

ACCESSION NR: AP5014580   UR/0181/65/007/006/1783/1786

AUTHOR: Sheka, V. I.

TITLE: Fine structure of the spectrum of a local center and exciton in semiconductors with extremum loops

SOURCE: Fizika tverdogo tela, v. 7, no. 6, 1965, 1783-1786

TOPIC TAGS: impurity level, spin orbit coupling, spectral fine structure, exciton, semiconductor band structure

ABSTRACT: The author calculates the splitting of the excited levels of a shallow impurity state, brought about by spin-orbit separation of the bands. This splitting is approximately equal to four times the depth of the extremum loop, multiplied by the magnetic quantum number. An analogous effect is determined for the exciton. The method used for the calculations makes it possible to take into account higher-order terms of the expansion in powers of

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ACCESSION NR: AP5014580   6

the ratio of the depth of the loop to the ionization potential of the center.
In the case of hexagonal CdS, the splitting is approximately equal to 10^{-4}ev,
as compared with 5×10^{-4}ev for the splitting of the exciton levels resulting
from the nonzero wave vector of light. "The author thanks E. I. Rashba for
suggesting the topic and a discussion of this work." Orig. art. has: 18
formulas.

ASSOCIATION: Institut poluprovodnikov AN UkrSSR, Kiev (Institute of Semi-
conductors AN UkrSSR)

SUBMITTED: 08Jan65   ENCL: 00   SUB CODE: 85, NP

NR REF SOV: 001   OTHER: 006

Card 2/2 DP

ACC NR: AP6037073   SOURCE CODE: UR/0056/66/051/ᵒ᛫᛫/1445/1456

AUTHOR: Sheka, V. I.; Sheka, D. I.

ORG: Institute of Semiconductors, Academy of Sciences, Ukrainian SSR (Institut polu-
provodnikov Akademii nauk Ukrainskoy SSR); Kiev State University (Kiyevskiy gosudar-
stvennyy universitet)

TITLE: Local states in semiconductors with narrow forbidden band

TOPIC TAGS: semiconductor band structure, impurity level, conduction band, valence
band, ionization, impurity center

ABSTRACT: A theory of impurity states in semiconductors having the same band struc-
ture as InSb is developed, within the framework of the scheme of E. O. Kane (Phys.
Chem. Sol. v. 1, 249, 1957), in a multiband approximation which takes into account
the interaction between the conduction and valence bands. By analyzing in detail the
band structure it is possible to calculate, in agreement with experiment, the ioniza-
tion energy of the acceptors and also to determine the wave function of the corres-
ponding state. A variational method is used to solve the equations of motion. The
changes occurring in the analytic structure of the solutions for the local center
when account is taken of the remote bands is also analyzed. The analysis indicates
that the behavior of the carrier near the acceptor center can be correctly described

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only if the upper bands are taken into account. The behavior of the carrier in the vicinity of the donor is practically independent of the equations of motion. The energy levels of large-radius local centers in InSb are determined numerically. The ionization potential thus obtained for the singly-charged acceptor center in InSb is in agreement with the experimental value. Several models of the band structure are presented for the case when the change in the system of singular points of the equations of motion makes it possible to obtain the exact solution. These include cases when the valence band is split by the spin-orbit interaction and is located above the bands of the light and heavy poles, when the spin-orbit splitting of the valence bands is eliminated, and others. The authors thank E. I. Rashba for constant interest in the work and a discussion. Orig. art. has: 3 figures and 33 formulas.

SUB CODE: 20/   SUBM DATE: 05May66/   ORIG REF: 008/   OTH REF: 006

Card 2/2

LEBEDEV, O. A.; FRANTAS'YEV, N. A.; OLYUNIN, G. V.; MUZHZHAVLEV, K. D.; SHEKA, V. P.; SHEKA, T. S.

Developing a method of mechanized removal of electrolytic slime in magnesium production. TSvet. met. 36 no. 11:38-41 N '63.   (MIRA 17:1)

MEZHZHAVLEV, K.D.; LEBEDEV, O.A.; FRANTAS'YEV, N.A.; OLYUNIN, G.V.;
        SHEKA, T.S.; LOIGIKH, T.K.; Prinimali uchastiye: POPOV, V.V.;
        SHEKA, V.P.

        Results of testing individual design elements of magnesium
        electrolytic cells. TSvet. met. 38 no.5:57-60 My '65.
                                                        (MIRA 18:6)

24.3500

68313

AUTHORS: Shpak, M.T. and Sheka, Ye.F.

SOV/51-8-1-12/40

TITLE: On the Intrinsic Luminescence of Crystalline Naphthalene

PERIODICAL: Optika i spektroskopiya, 1960, Vol 8, Nr 1, pp 66-72 (USSR)

ABSTRACT: The authors investigated the luminescence spectrum of crystalline
naphthalene lying in the region of fundamental absorption. The
luminescence and absorption spectra were obtained at 20.4, 77,
200-210, 293 and 330-340°K. Medium-dispersion quartz spectrographs
ISP-22 and Hilger E-2 were used. For the absorption spectra a
krypton lamp GSVD-120 was used; luminescence was excited with
2530-2400 Å light from a mercury lamp SVDSh-1000. A Glan-Thomson
prism was used as an analyser. Very pure samples of naphthalene
were obtained by repeated zone purification (45 runs). Purity of
the samples was judged by the absence of β-methyl naphthalene bands
in the absorption spectrum. Fig 1 gives the luminescence spectra of
naphthalene crystals at 20.4°K. Fig 1 shows a luminescence band at
31480 ± 3 cm^{-1} weakly polarized along the a-direction (this is called
an A-band). The A-band practically coincides with a strongly polarized
A_1-band at 31479 cm^{-1} in the absorption spectrum (Ref 11). The A-band
is more intense in purer samples. On increase of temperature to 77°K

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On the Intrinsic Luminescence of Crystalline Naphthalene

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another band appears in the luminescence spectrum; it lies at
31623 ± 3 cm^{-1} (the B-band) and it is polarized in the b-direction
(Fig 2). At 200-210°K (Fig 3) the A- and B-bands are broader and
partly depolarized (they coincide with the A_1-and B_1-bands in the
absorption spectrum at the same temperature). At 200-210°K a very weak
luminescence band (the I-band) appears at 31900 cm^{-1}. On increase of
temperature to 293°K the A- and B-bands are depolarized still further
(the spectrum is practically unaffected by a 90° rotation of the
Glan-Thomson prism) and the intensity of the I-band rises (Fig 4a).
The I-band is also completely depolarized. At 330-340°K the A-, B-
and I-bands become stronger and another band appears in the spectrum
(the II-band), which lies in the region of the A_2 and B_2 absorption
bands (Ref 11). Rise of temperature depolarizes also the absorption
bands which are strongly polarized at 20.4°K (Fig 5). At 77°K a new
band (the III-band) is observed in the absorption spectra of thick
naphthalene crystals; this band lies at 31100 cm^{-1} and its intensity

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On the Intrinsic Luminescence of Crystalline Naphthalene   SOV/51-8-1-12/40

rises on increase of temperature. At 330-340°K no further changes are
observed in the absorption spectrum. The authors show that the results
point to exciton nature of luminescence of very pure naphthalene
crystals in the region of fundamental absorption. Acknowledgment is
made to A.F. Prikhot'ko for his advice. There are 5 figures and
14 references, 9 of which are Soviet, 3 English and 2 German.

SUBMITTED: June 8, 1959

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24.3500

81915

S/051/60/009/01/010/031
E201/E691

AUTHORS: Shpak, M.T. and Sheka, Ye.F.

TITLE: The Effect of Impurities on Luminescence of Crystalline Naphthalene

PERIODICAL: Optika i spektroskopiya, 1960, Vol 9, Nr 1, pp 57-63 (USSR)

ABSTRACT: Earlier Prikhot'ko and Shpak (Ref 1) showed that luminescence of
crystalline naphthalene (Ref 2) is due to a β-methylnaphthalene
impurity. It was also reported that crystalline naphthalene contains
small amounts of α-naphthol, β-naphthol, thionaphthene and other
substances. The present paper reports an investigation of the
effect of temperature and solute (impurity) concentration on the
luminescence and absorption spectra of solid solutions of
β-methylnaphthalene, α-methylnaphthalene, β-naphthol and α-naphthol
in crystalline naphthalene. The experimental technique was the same
as described earlier (Ref 3). The experiments were carried out
at 20.4, 77 and 200°K. The results (Figs 1-5 and Tables 1-4) showed

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The Effect of Impurities on Luminescence of Crystalline Naphthalene

that solute molecules produced two types of luminescence centres
in the naphthalene lattice.   Acknowledgments are made to
A.F. Prikhot'ko for his advice and to a graduate of the Kiyev State
University, Ye G. Ruseva.   There are 5 figures, 4 tables and
11 references, 8 of which are Soviet, 2 English and 1 German.

SUBMITTED: September 18, 1959

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SHPAK, M.T.; SHEKA, Ye.F.

Luminescence of crystalline naphthalene containing minor admix-
tures.   Izv.AN SSSR.Ser.fiz. 24 no.5:553-555 My '60.
(MIRA 13:5)

1. Institut fiziki AN USSR.
          (Naphthalene--Optical properties)

SHEKA, Ye.F.

Nature of the first bands of the main absorption spectrum of
a naphthalene crystal. Opt.i spektr. 10 no.5:684-686 My '61.

(Naphthalene crystals--Spectra)

(MIRA 14:8)

27257

24 4400   1158   1395 also 1160 1462

S/020/61/139/005/007/021
B104/B201

AUTHORS: Broude, V. L., Rashba, E. I., and Sheka, Ye. F.

TITLE: Anomalous impurity absorption near exciton bands of
             molecular crystals

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 5, 1961, 1085-
             1088

TEXT: If, in a molecular crystal, the distance $\mathcal{E}$ of an impurity level
from the edge of the exciton band is smaller than, or is of the same
order of magnitude of the width M of the exciton band, an absorption of
light within the range of the impurity band will lead to the formation
of quantum states, in which not only the impurity molecule, but also the
adjoining molecule of the solvent will be excited. For $\mathcal{E} \lessgtr M$, the
dimensions of the regions in which the excitation is concentrated, are
larger than the lattice constant. The structure of the exciton band
near its edge displays an influence upon the characteristics of impurity
absorption. If, in this case, the impurity molecule does not differ
from a molecule of the solvent except by a shift of energy levels,

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Anomalous impurity absorption near ...

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impurity absorption will diminish as $\xi^{1/2}$ if an optical transition to the edge of the exciton band with a given polarization of light is forbidden, or will grow as $\xi^{-3/2}$ if such a transition is allowed. Thus, the coefficients of these relations are sharply dependent upon ξ, and so are the polarization relations; for $\xi \leq M$, ξ itself is a function of the distance 2f between the levels of the molecule of the solvent and the impurity molecules. Thus, the characteristics of impurity absorption permit conclusions to be drawn regarding the structure of exciton bands. Objects suited for these investigations are molecular crystals, in which the molecules of the solvent do not differ from the impurity molecules except by their isotopic composition. Solutions of ordinary naphthalene $(C_{10}H_8)$ in octadeuteronaphthalene $(C_{10}D_8)$ and in tetradeuteronaphthalene $(\measuredangle-C_{10}D_4H_4$ and $\beta-C_{10}D_4H_4)$ have been studied. These preparations were supplied to the authors by Professor A. I. Shatenshteyn, and had been prepared in his laboratory at the Institut fizicheskoy khimii im. L. A. Karpova (Institute of Physical Chemistry imeni L. A. Karpov). The naphthalene concentration amounted to some percents. The effects observed are in agreement with those theoretically predicted by E. I. Rashba

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